

Helicene-grafted vinyl- and carbene-osmium complexes: an example of acid-base chiroptical switching

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The first helicene-based carbene osmium complex has been prepared from a vinyl-osmium derivative and this system has been shown to behave as a potential acid-base triggered chiroptical switch.

Helicene derivatives have recently shown potential as molecular materials due to their inherent chirality, large magnitude chiroptical properties and π -conjugated electronic structure.¹ For example, they have revealed fascinating optical, redox or chemical-stimuli induced chiroptical switching.^{2,3} These compounds may find applications in various domains such as in optical displays, telecommunications, or molecular electronics. The design of new types of functional chiral molecular switches is needed and in this context, the switching of chiral metal-based systems has great potential,^{2c} due to the possibility of reversibly modifying the molecule by changing the metal center's properties (geometry, redox state, ...).^{2c,d} In this communication, we describe the synthesis of an unprecedented enantiopure carbene-osmium helicene complex from an enantiopure helicene-grafted vinyl-osmium derivative. The potential use of these chiral organometallic systems as acid-base chiroptical switches is examined. The electronic interaction between the vinyl-osmium or carbene-osmium units and the carbo[6]helicene core is investigated by DFT calculations.

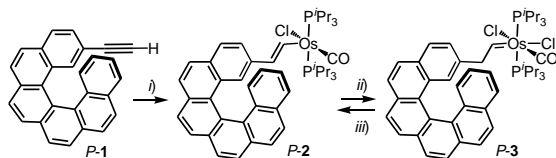
Enantiopure vinyl-osmium-helicene complexes *M*- and *P*-2 (Scheme 1) were prepared in good yield (65-70%) using a known procedure,⁴ *i.e.* by hydro-osmylation of enantiopure *M*-(-) and *P*-(+)-1 with 1 equivalent of OsHCl(P^{*i*}Pr₃)₂ in CH₂Cl₂ at room temperature (r.t.). The NMR data fully support the proposed structure in accordance with previously reported analogues.⁴ For instance, the ¹H NMR spectrum of **2** displays the fingerprint for *trans*-ethylene metal-substituted moieties with a doublet of triplets at 4.80 ppm (³J_{H-H} = 13.4 Hz, ³J_{P-H} = 1.8 Hz) corresponding to the proton in the β position of the osmium center. Furthermore, according to ³¹P NMR spectroscopy the two P^{*i*}Pr₃ ligands are non-equivalent (23.96 and 23.92 ppm), indicating slightly different chemical environments for the two fragments. The X-ray structure of

Scheme 1. Synthesis of enantiopure helicene-grafted vinyl-osmium complex *P*-2 and osmium-carbene *P*-3 from enantiopure *P*-1. *i*) HOs(CO)Cl(P^{*i*}Pr₃)₂, CH₂Cl₂, r.t., Ar, 3 days, 70%. *ii*) HCl, toluene, 10 min., 86%. *iii*) NEt₃, CH₂Cl₂.

complex **2** (Figure 1) reveals a square pyramidal pentacoordinated osmium center in which the two *trans* P^{*i*}Pr₃ ligands, Cl and CO form the basis of the pyramid and the vinyl-helicene ligand is at the apical position. The Os-C1-C2-C3 bond lengths (1.987, 1.343 and 1.453 Å) are indicative of a *trans* vinyl-Os moiety that is almost coplanar with the helicene part (Os-C1-C2-C3, 176.53°), allowing an efficient π -interaction of the helicene ligand with the Os center. The helical angle (angle between the terminal rings of the helix, 50.3°) is similar to reported values for other metal-helicene compounds.^{3a} Overall, complex **2** is isostructural to its Ru analogue^{3a,4b} but osmium complexes are usually less easy to handle due to a lower stability.

Complexes containing Os=C(H)R units have been prepared.^{4a-e} Such carbene complexes (also named alkylidene-osmium complexes) are an important class of compounds but to our knowledge their electronic and chiroptical properties have not yet been studied. The first enantiopure helicene-based carbene-osmium complexes *M*- and *P*-3 (Scheme 1) were straightforwardly prepared from vinyl-osmium complexes *M*- and *P*-2 by a simple addition of slight excess of HCl in toluene at r.t.^{4a} and characterized by ¹H, ³¹P{¹H} and ¹³C{¹H} NMR, along with IR, UV-vis and ECD spectroscopies. For example, the ¹H NMR spectrum of mono-carbene **3** in CD₂Cl₂ showed the presence of a triplet at 18.1 ppm (³J_{HH} = 6.6 Hz) which is typical of the CH=Os and two doublets of doublets at 2.85 and 3.13 ppm corresponding to the methylene group. In the ¹³C{¹H} NMR spectrum, the *sp*² carbon appears as a doublet of doublet (²J_{CP} = 8.5 Hz) at 296.7 ppm. Furthermore, two singlets at 12.89 and 12.47 ppm are found in the ³¹P{¹H} NMR spectrum. These are typical values for aryl-methylene-carbene-osmium species^{4a} and correspond to the two P atoms in different chemical environments. Note that in such complexes the osmium centers are octahedral with a coordination sphere completed by a chloride ligand (see optimized structure in Figure 2). The Os-C1-C2-C3 dihedral angle in the calculated structure of **3** is 159.35°, which indicates a rotation of the helicene moiety around C1-C2 axis as compared to **2**. See Supplementary Information, SI, for Cartesian coordinates of both calculated structures **2** and **3**.

Vinyl-osmium helicene complex **2** displays two strong high-energy absorption bands (258 and 314 nm, $\epsilon \sim 70 \cdot 10^3$ M⁻¹ cm⁻¹ and $45 \cdot 10^3$ M⁻¹ cm⁻¹, respectively, see SI) that originate from the π -system of the



helicene ligand, along with a broad low-energy band at 405 nm of moderate intensity ($\epsilon \sim 14 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) that does not exist in ligand **1** and is due to efficient electronic interaction between the vinyl-osmium moiety and the helicenic π -core (see below). Interestingly, the carbene-osmium complex **3** displays the same high-energy absorption bands as **2** for the π - π^* transition of the helicene-core while the low-energy band at 405 nm has disappeared and two new broad bands of low intensity are found at 500 nm ($\epsilon \sim 5 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 785 nm ($\epsilon \sim 3 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), see SI. In addition, enantiopure complexes *M*- and *P*-**2** display molar rotation (MR) values that are much higher than the corresponding ligand **1** ($[\phi]_D^{25}$ in $^\circ\text{cm}^2/\text{dmol}$: *P*-**2**: +18000 vs. *P*-**1**: +11030). The circular dichroism (CD) spectrum of the complex *P*-**2** depicted in Figure 1 shows, aside from the regular strong bands present in the helicene core, new ECD-active bands between 380–480 nm as compared with the ethynyl-substituted precursor *P*-**1**. These new bands involve electronic interaction between the vinyl-metal-center and the helical π -system as confirmed by density functional calculations performed at the BHLYP/SV(P) level (see SI for Computational Details). For example, calculated excitations *n* \rightarrow 3 (367 nm) and *n* \rightarrow 4 (354 nm) manifest character of π to π^* transitions within the helicene ligand (HOMO–LUMO: 65% and HOMO–LUMO+1: 60%, respectively; see Figure 2 and SI). Both excitations are at low energy / long wavelength, due to an enlargement of the helicene chromophore by conjugation through the vinyl bridge and osmium *d* orbital involvement. Yet, because of the chirality of the helicene moiety, the transitions carry significant rotatory strength and contribute predominantly to the positive CD intensity at long wavelengths. In addition, a metal-centered excitation (*n* \rightarrow 2, 373 nm, HOMO–4–LUMO+2: 78%) with moderate rotatory strength is present at lower energy. The resulting intense low-energy tail of the first positive ECD band is responsible for the increase in the molar rotation of the metal-grafted vinyl-helicene derivatives compared to the free ligands. Indeed, the calculated MR values of the *P*-isomers (**2**: 23915 with BHLYP and 17435 $^\circ\text{cm}^2/\text{dmol}$ with LC-PBE0) reproduce well the strong increase relative to the helicene ligand (**1**: 17002 (BHLYP) and 13800 $^\circ\text{cm}^2/\text{dmol}$ (LC-PBE0)). See ref. 5 and SI for more details.

The osmium-carbene-helicene derivative revealed $[\phi]_D^{25}$ values close to those of the ligands ($[\phi]_D^{25}$ in $^\circ\text{cm}^2/\text{dmol}$: *P*-**3**: +9600 vs. *P*-**1**: +11030). The ECD spectrum of complex *P*-**3** shows a sharp negative band at 250 nm and a sharp positive one at 330 nm (Figure 1). Additionally, new weakly ECD-active bands at 500 and 785 nm ($\Delta\epsilon \sim 3\text{--}14 \text{ M}^{-1} \text{ cm}^{-1}$) are also present in *P*-**3**. TDDFT calculations on the singlet osmium carbene complex reproduced well the high-energy strong positive ECD-active bands in *P*-**3** originating from the purely helicenic π - π^* transitions (excitation *n* \rightarrow 5, 309 nm, HOMO–LUMO+2: 50% and HOMO–1–LUMO: 35%, see Figure 2 and SI), calculated in the same energy range where the strongest rotatory strength excitation of its organic precursor **1** occurs. As depicted in Figure 2 and SI, for **3** these MOs are centered on the π -helical core without visible involvement of the osmium *d* orbitals. Unlike complex **2**, it appears that in the carbene-osmium derivative **3** the electronic coupling between metal center and the helicoidal π -system is broken due to the presence of the CH_2 .

Figure 1. CD spectra of *P*-**1a** (blue) vs. *P*-**2** (red) and *P*-**3** (black) in CH_2Cl_2 (C 1–5 10^{-5} M^{-1}). Inserts: low-energy CD spectra of *P*-**2**, **3**. X-ray structure of complex **2** (one enantiomer shown).

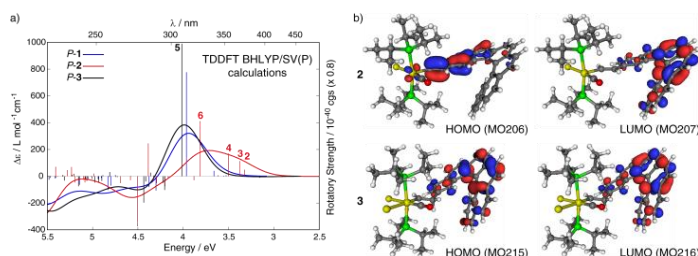
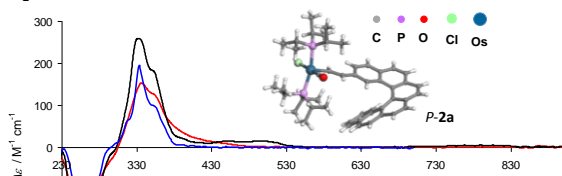


Figure 2. a) Calculated CD spectra of *P*-**1** (blue), *P*-**2** (red), and *P*-**3** (black) BHLYP/SV(P). b) Iso-surfaces (0.04 au) of frontier MOs of **2** and **3**.

Despite of the correct description of the high-energy part of the CD spectrum of **3**, the very weak low-energy ECD-active bands could not be reproduced by a variety of non spin-orbit calculations. Absorptions to triplet excited states are often observed in heavy metal complexes because spin-orbit coupling weakens the spin selection rules.⁶ Calculations did indeed show the presence of triplet excitations in the wavelength range of interest. However, the appearance of triplet transitions above 600 nm was dependent on various approximations⁷ (see SI for more details).⁸ The calculated MR values of **3** were found to be overestimated as compared to the experimental result (17557 with BHLYP and 14173 with LC-PBE0) and similar to the calculated MR of **1**. The trend among the set of complexes is thus correctly reproduced by the calculations. Another interesting question pertaining the electronic structure of **3** is the presence or absence of hyperconjugation (σ - π conjugation between CH_2 and $\text{C}=\text{Os}$ or helicene) which may affect structure and bonding in metal carbene complexes⁹ and leave signatures in UV-vis spectra.¹⁰ The optimized BP/SV(P) geometry of **3** does however not exhibit structural features that usually would be identified with hyperconjugation.^{9,4a}

The ability of the helicene-osmium system to behave as an acid-base switch was examined. The reversible formation of helicene-vinyl-osmium *P*-**2** from a solution of osmium-carbene-helicene *P*-**3** in CH_2Cl_2 was performed by simply using NEt_3 and the UV-vis and ECD spectra of *P*-**2** were almost recovered (see SI). Furthermore, the IR spectra of complexes **2** showed a characteristic CO stretching mode (ν_{CO}) at $\sim 1895 \text{ cm}^{-1}$ that disappears upon adding HCl in toluene, while a new band grew up at $\sim 1932 \text{ cm}^{-1}$ corresponding to **3**. This shows a stronger donating character of the helicene-vinyl ligand compared to the carbene. The reverse transformation to **2** could be conducted by using NEt_3 as followed by their IR ν_{CO} (Figure 3). This transformation is thought to involve a deprotonation of the acidic CH_2 group by the base



followed by a 1,3-shift leading to HCl abstraction.^{4f} As a consequence, this molecular system acts as an acid-base triggered chiroptical switch since the several ECD bands (330 nm, 800 nm, ...) are greatly modified upon **2** \rightleftharpoons **3** transformation. Although the system is not practically efficient due to the low stability of highly diluted solutions of carbene-osmium derivatives,[#] to our knowledge this is the first time that a carbene derivative is used as a chiroptical switch.

In conclusion, the first enantiopure carbene-osmium based helicene derivative (**3**) has been prepared from unprecedented vinyl-osmium helicene derivative (**2**). The examination of the reversible transformation from **2** \rightleftharpoons **3** enabled to set up a new kind of an acid-base chiroptical switch due to the modification of the electronic interaction between the π -helical core and a grafted osmium moiety. This example illustrates the inspiration from simple and well-known organometallic chemistry to the design of new kinds of helicene-based molecular switching systems.

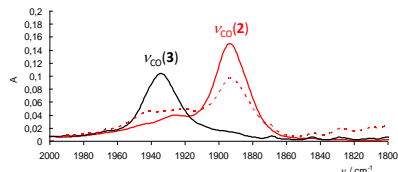


Figure 3. Reversibility test of the (carbene/vinyl)-osmium **2** \rightleftharpoons **3** transformation. IR spectra in CH₂Cl₂ solution in the 1800–200 cm^{−1} region (ν_{CO} stretching band). Spectrum obtained after **3** \rightarrow **2** transformation is indicated in dashed red lines.

Notes and references

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#Complex **3** is stable for several months if kept under rigorously inert atmosphere. However, it was not practically feasible to perform several reversible cycles due to successive adding of reagents in the solution and therefore changes in concentrations.

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